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In re Application of: **Rabah BOUKHERROUB**

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For: PASSIVATION OF POROUS SEMICONDUCTORS

MAIL STOP AF

Commissioner of Patent and Trademarks

P.O. Box 1450, Alexandria, Virginia 22313-1450

Declaration under 37 CFR 1.131

We, the undersigned, are the named inventors in respect of the above-referenced application, and do hereby declare as follows:

1. Independent claims 1 and 19 of the application as currently on file are directed toward a method of stabilizing porous silicon wherein a porous silicon substrate is subjected to thermal processing with reactants from a group including aldehydes.

USSN: 10/830,035

Art Unit: 1765

Declaration under 37 CFR 1.131

2. We made and reduced the invention
3. and reduced the invention defined by claims 1 and 19 to practice at least as early as March 12, 2000 when the attached paper marked as exhibit 1 and entitled "Thermal Route for Chemical Modification and Photoluminescence Stabilization of Porous Silicon" was submitted for publication to Physica Status Solidi (a). The paper was subsequently published on November 28, 2000 in Volume 182, Issue 1, Pages 117 – 121.
4. In this paper we discuss the thermal reaction of alkenes and aldehydes with H-terminated PSi surfaces, and conclude on page 5 that "This chemical process effectively protects the PSi surface against the PL fatigue even in very aggressive environments."
5. Further evidence of our work is contained in the article marked exhibit 2 and entitled "pickled Luminescent Porous Silicon", which was submitted to the journal Solid State Communications on January 29, 2001, and therefore establishes an invention date in respect of the subject matter it contains at least as early as January 29, 2001.
6. The remaining compounds covered by claims 1 and 19 and not disclosed in the above papers can be predicted from the results set forth in those papers.
7. Subsequent to the preparation of the above papers, at no time did we abandon our invention.
8. We hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed

Date:

USSN: 10/830,035
Art Unit: 1765
Declaration under 37 CFR 1.131

Rabah Boukherroub

Signed

Date:

Daniel D. M. Wayner

Signed



Date: 25 October 2006

David J. Lockwood

Signed

Date:

Sylvie Morin

Thermal Route for Chemical Modification and Photoluminescence Stabilization of Porous Silicon.

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Contribution from [†]Steacie Institute for Molecular Sciences and [§]Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

Subject classification: 68.90.+g; 78.30.Jw; 78.55.Mb; S5.11; S12.

Abstract: This paper describes photoluminescence (PL) stabilization through chemical modification of the freshly prepared porous silicon (PSi) surfaces. As-anodized PSi surfaces react with 1-alkenes, non-conjugated dienes and aldehydes at elevated temperatures to form organic monolayers covalently bonded to the surface. This thermal route is very general and tolerant of different functional groups. We have characterized these organic monolayers using DRIFT, Auger and Raman spectroscopies. The PL of the as-anodized PSi is not affected by the chemical functionalization. The modified samples have shown comparable intensity and peak energy to those of H-terminated PSi. Aging these derivatized PSi samples in ambient air has no effect on the PL. In fact, it is completely preserved even when they are steam treated for 6 weeks at 70°C at a 100% humidity. This treatment completely destroyed the structural integrity of the H-terminated PSi.

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1- Introduction

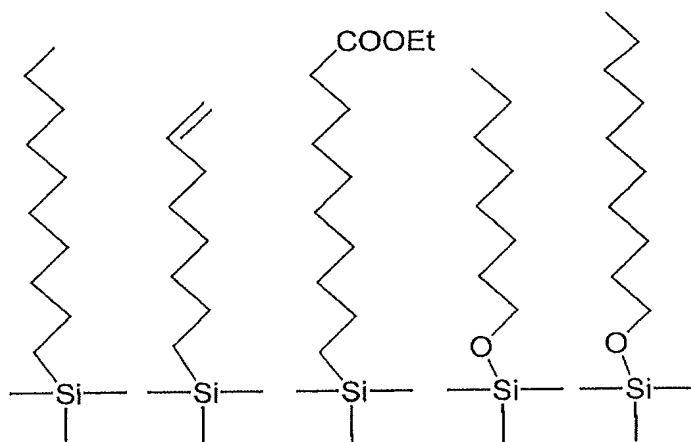
Porous silicon (PSi) is an interesting material prepared by chemical or electrochemical etching of bulk silicon in HF-based solutions [1]. It is a complex network of nanostructures and shows photoluminescent properties when excited with UV light [2]. The origin of the PL has been a subject of controversy but is now believed to result from quantum confinement within the nanospheres, in the porous structure [1]. Freshly prepared PSi is passivated with a monolayer of hydrogen. This monolayer offers good electronic properties to the material but suffers from its long-term instability. A slow oxidation occurs when the PSi is exposed to ambient air and results in photoluminescence (PL) degradation. This process may be accelerated upon exposure to UV light [3].

A significant amount of research has been directed towards the discovery of methods to stabilize the PL of PSi for potential applications in optoelectronics. Different methods to stabilize the H-terminated surface have been proposed in the literature in order to preserve the PSi from PL fatigue [4]. More recently, organic modification has emerged as an alternative to achieve this goal [5]. Formation of organic monolayers containing silicon-carbon bonds on the surface should improve the resistance of the surface to oxidation because of the high stability of the Si-C bond in different media. We have reported that organic monolayers formed on a single crystal by a direct reaction of Si(111)-H with Grignard reagents [6] and aldehydes [7] are very robust. We have also shown that further manipulations of the end functional groups are achievable with high yields [8].

In this paper, we report a thermal hydrosilylation of PSi surfaces with 1-decene [9], 1,7-octadiene, ethylundecylenate, and octyl and decyl aldehydes. The functionalized surfaces were characterized using DRIFT, Auger, and Raman spectroscopies. We have studied the aging effect on the PL of the H-terminated and decyl-terminated surfaces in air and in a more aggressive environment (steam treatment at 70°C) for several weeks. Surfaces prepared in this way are compared to those formed by catalytic hydrosilylation [Buriak, 1999]

2- Results and discussion

Reaction of H-terminated PSi with 1-decene, 1,7-octadiene, ethylundecylenate, octyl and decyl aldehydes at elevated temperatures (85-115°C) gives organic monolayers covalently-attached to the surface. We have prepared different monolayers by this method (scheme 1):



Scheme 1

DRIFT spectrum of freshly prepared PSi sample consists on Si-H_x stretch modes at 2117 cm⁻¹ and scissor mode at 918 cm⁻¹. The peak at 1031 cm⁻¹, which is present in all PSi samples, is due to the interstitial oxygen within the silicon lattice (figure 1a). Modification with 1,7-octadiene (figure 1b) introduces additional peaks at 2927 cm⁻¹ due to C-H stretching. The presence of the terminal double bond is confirmed by the stretching at 3080 cm⁻¹ and 1644 cm⁻¹ corresponding to the stretching modes of the ethylenic C-H and the C=C double bond respectively. Figure 1c displays the spectrum of a modified PSi with 1-decene. Absorptions due to the C-H stretching modes of the alkyl chain and methylene bending modes appear at 2918 cm⁻¹ and 1470 cm⁻¹ respectively. There are no absorptions related to the double bond, which is consistent with a covalent attachment of the organic monolayer without any apparent physisorbed molecules. The silicon-hydrogen absorption becomes broad and featureless. This phenomenon is due to interactions of the remaining Si-H_x with the neighbouring organic molecules attached to the surface. A similar effect was reported when organic molecules are physisorbed on the Si(111)-H [10, 11]. The Si-H_x intensity decreases substantially after the chemical modification. This indicates that the reaction takes place with hydrogen consumption. For the reaction of 1-decene approximately 70 percent of the Si-H groups react. A similar reaction under catalytic conditions leads to the consumption of only 30 percent of the Si-H groups [Buriak, 1999].

Figure 2a exhibits the Auger profile of the modified PSi surface with 1-decene. A constant atomic concentration of silicon and carbon throughout the pores was observed. The atomic concentration of oxygen is very low, which is consistent with a reaction without any oxidation of the surface. This result is very significant with respect to the efficiency of the reaction as it shows that the reaction occurs not only at the surface but also within the internal parts of the porous layer.

Modified PSi samples retain 40 to 80% of the freshly-prepared PSi PL intensity. The PL peak energy is not affected by the chemical derivatization (the maximum is centered at 1.8 eV as expected for a 70% porosity PSi). Aging the samples in air, in the dark or exposed to the day light has no effect on the PL and no spectroscopic changes have been noticed after two months. Even when subjected to more aggressive treatment (100 percent humidity at 70°C for several weeks) the sample modified with 1-decene (figure 4) showed an increase of the PL intensity of only a factor of 3 while the H-terminated PSi in the same conditions had increased by a factor of 50 (figure 5). The increase in PL has been assigned to a chemical oxidation of the PSi surface [12].

In order to understand and quantify the aging effect on the structural aspects of the porous layer, we have used Raman spectroscopy as a tool to monitor these changes. Raman spectrum of H-terminated PSi (figure 6b) exhibits an asymmetric second order silicon peak at 516 cm^{-1} . The decyl-terminated surface is similar in shape and position with a lower intensity (30% lower than the H-terminated PSi). Figure 6a corresponds to second order Raman silicon peak of the functionalized surface with 1-decene after steam treatment for 6 weeks. It is similar to the freshly-prepared decyl-terminated PSi, which indicates that the steam did not affect the porous layer integrity. The H-terminated PSi in contrast gave a new symmetric silicon peak centered at 520 cm^{-1} typical of crystalline silicon, in the same conditions. The porous layer is thus converted to a transparent layer of silicon oxide SiO_x (figure 6c). These observations were confirmed by DRIFT and X-ray photoelectron spectroscopies and demonstrate the extreme stability of the modified surfaces and the effective protection of the porous silicon structure.

3- Conclusion

We have shown that thermal reaction of alkenes and aldehydes with H-terminated PSi surfaces takes place at elevated temperatures to give organic monolayers covalently-bonded to

the surface. This chemical process effectively protects the PSi surfaces against the PL fatigue even in very aggressive environments. This method is straight forward to carry out and allows one to incorporate a variety of functional groups. The ease with which these highly stable monolayers are formed and the possibility of carrying out further manipulations of the end functional groups are important steps toward the development of photonic and sensing devices.

4- References

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Figure captions

Figure 1: Diffuse reflectance infrared Fourier-transform spectra of a) freshly prepared PSi before derivatization, and after functionalization with b) 1,7-octadiene and c) 1-decene.

Figure 2: Auger profile of PSi modified with 1-decene

Figure 3: Steady-state room temperature PL spectra of a) freshly-prepared PSi, functionalized PSi surfaces with b) octyl aldehyde, c) decyl aldehyde, and d) 1-decene.

Figure 4: Photoluminescence of the modified PSi surface with 1-decene a) before and b) after steam treatment for 6 weeks.

Figure 5: PL of the freshly prepared PSi a) before and b) after steam treatment.

Figure 6: Raman spectra of the silicon (Si) peak of a) decyl-modified surface after steam treatment, and freshly prepared PSi b) before and c) after steam treatment.

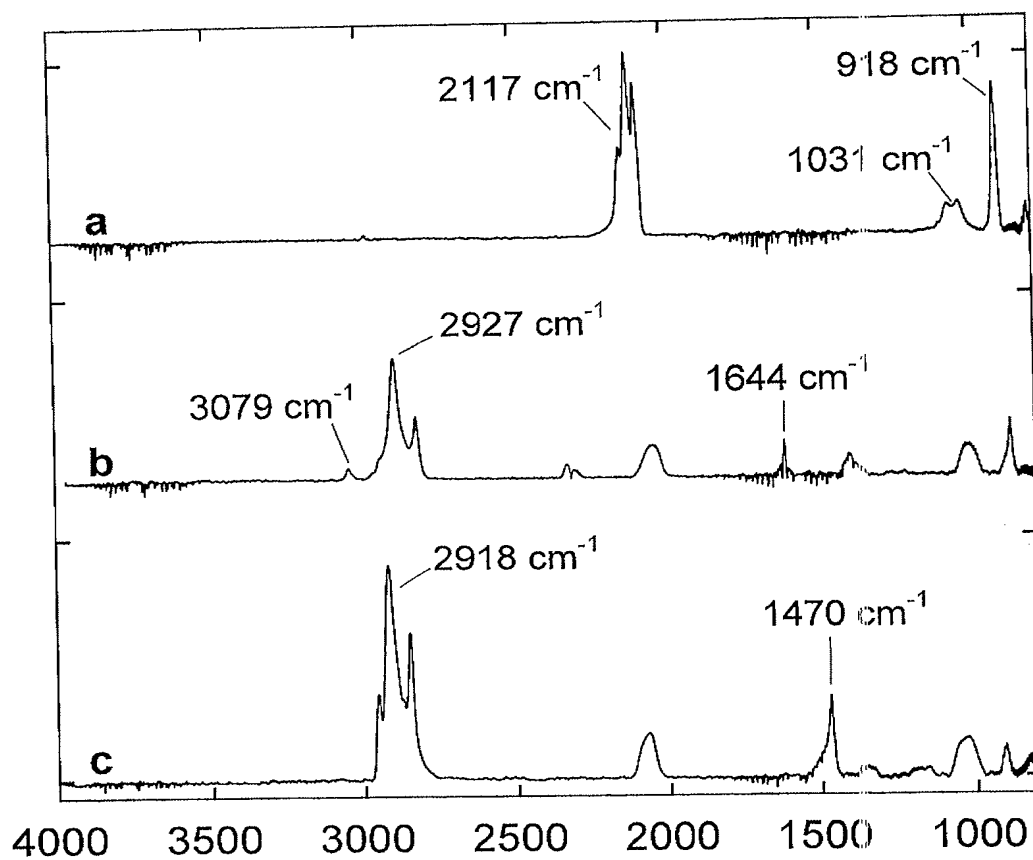


Figure 1

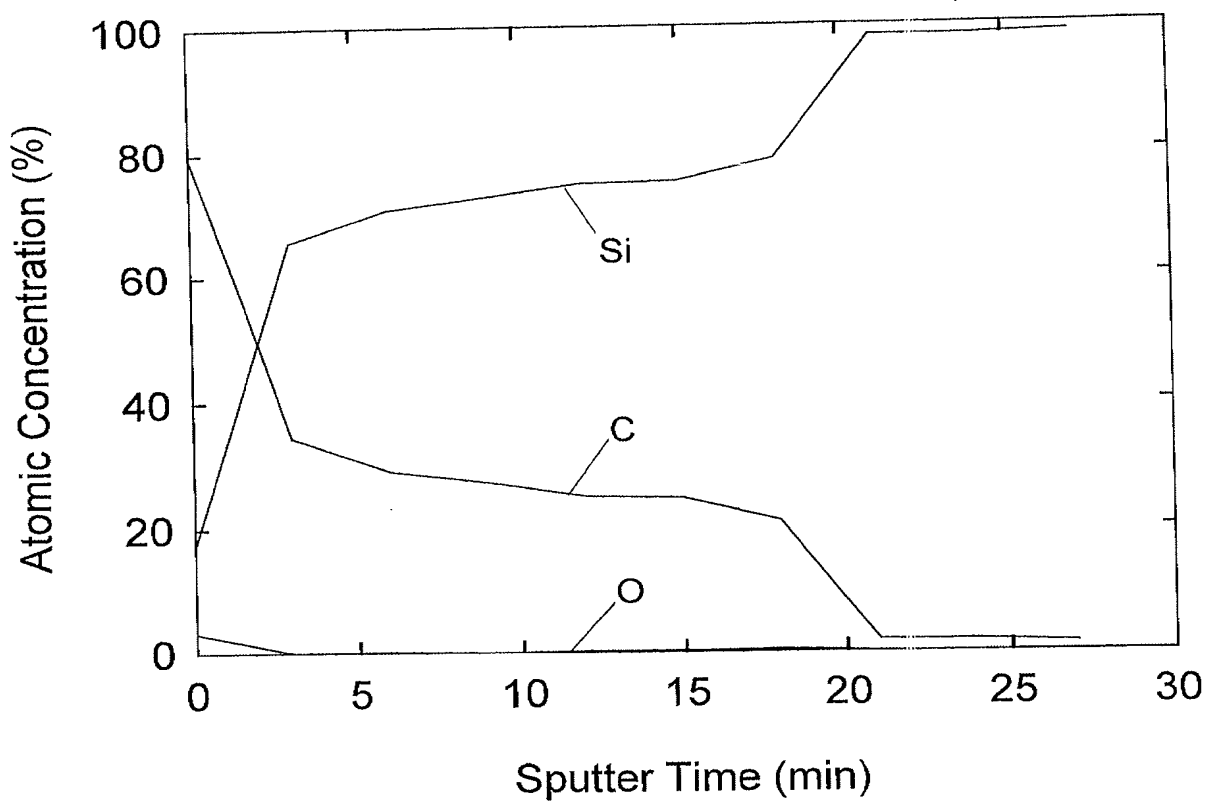


Figure 2

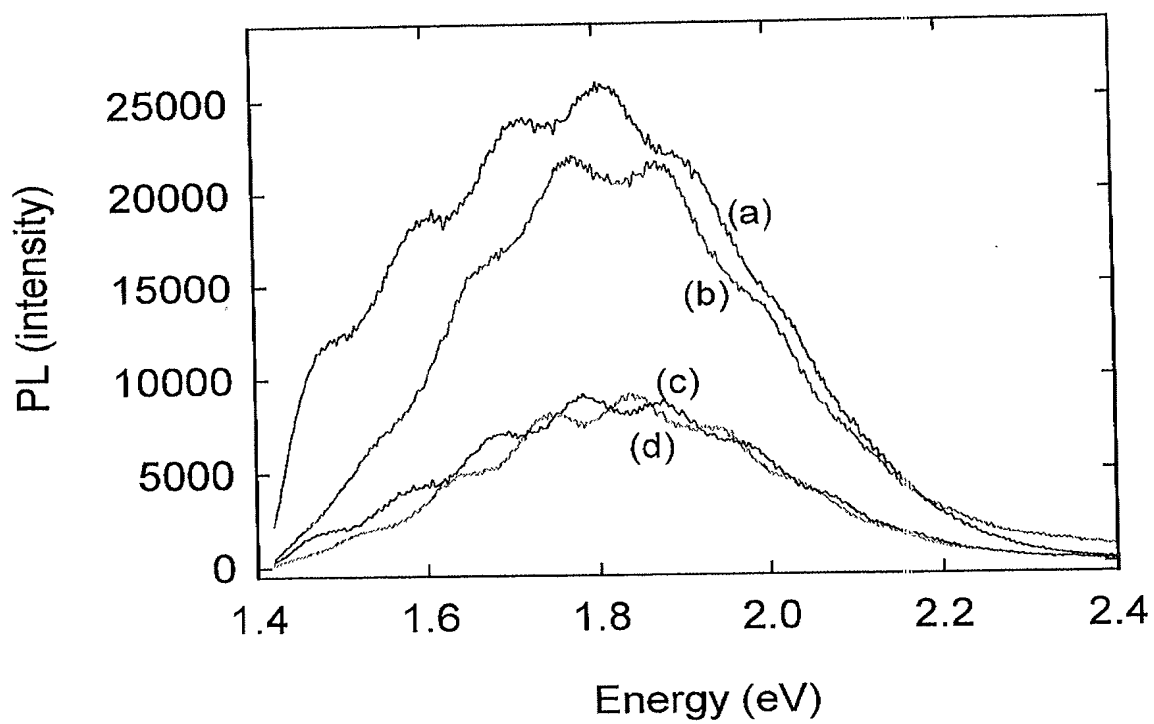


Figure 3

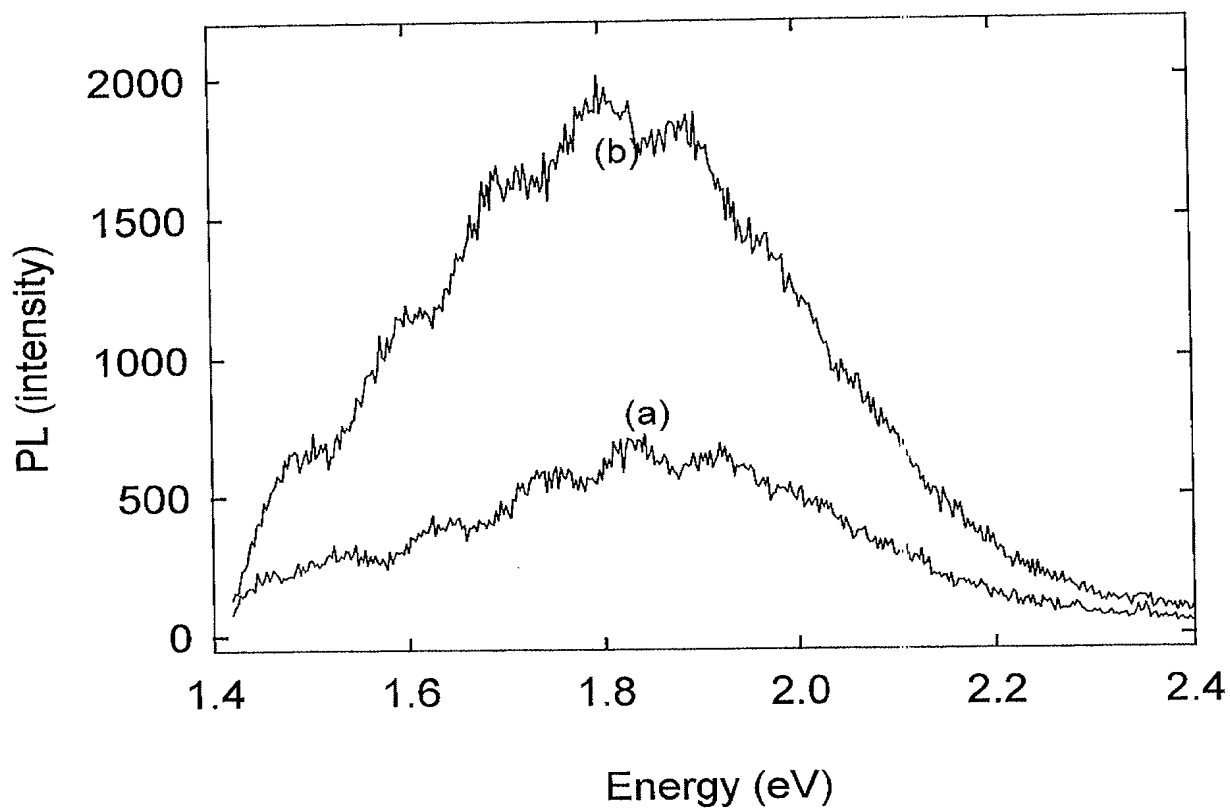


Figure 4

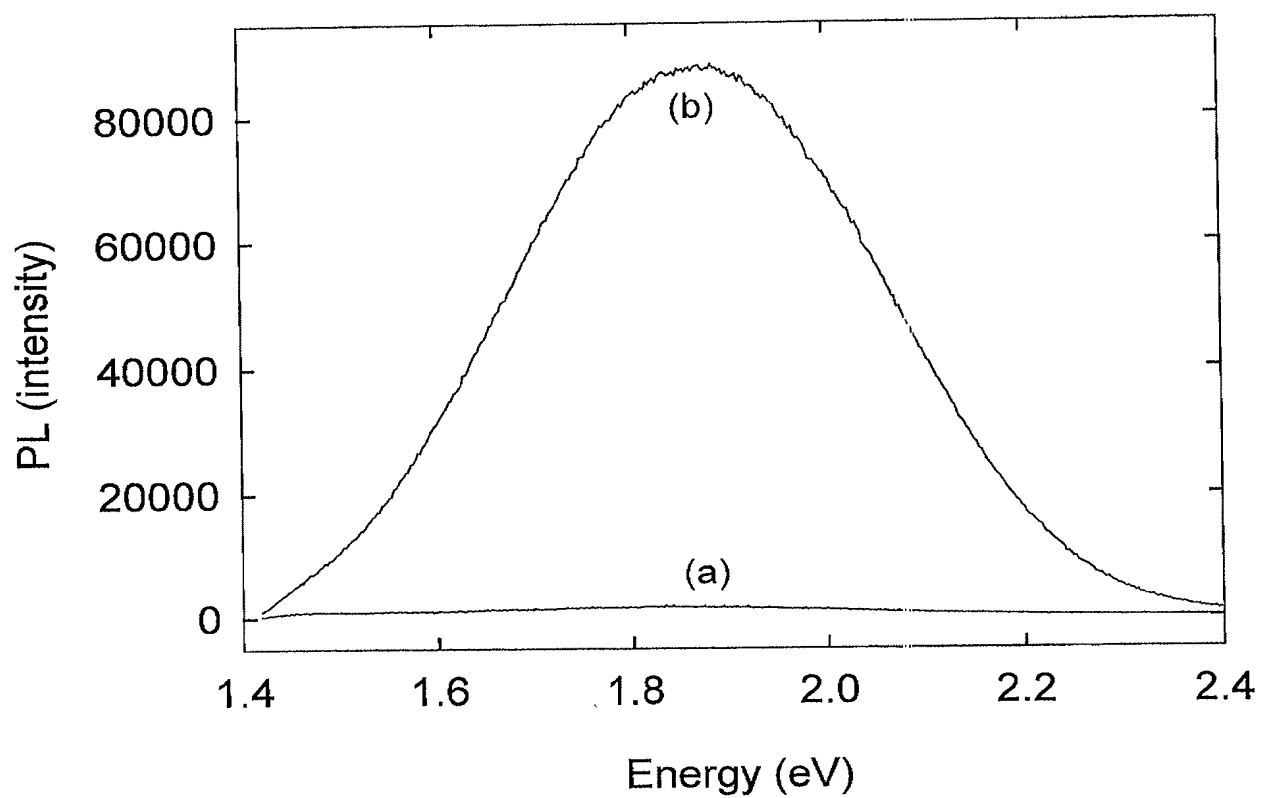


Figure 5

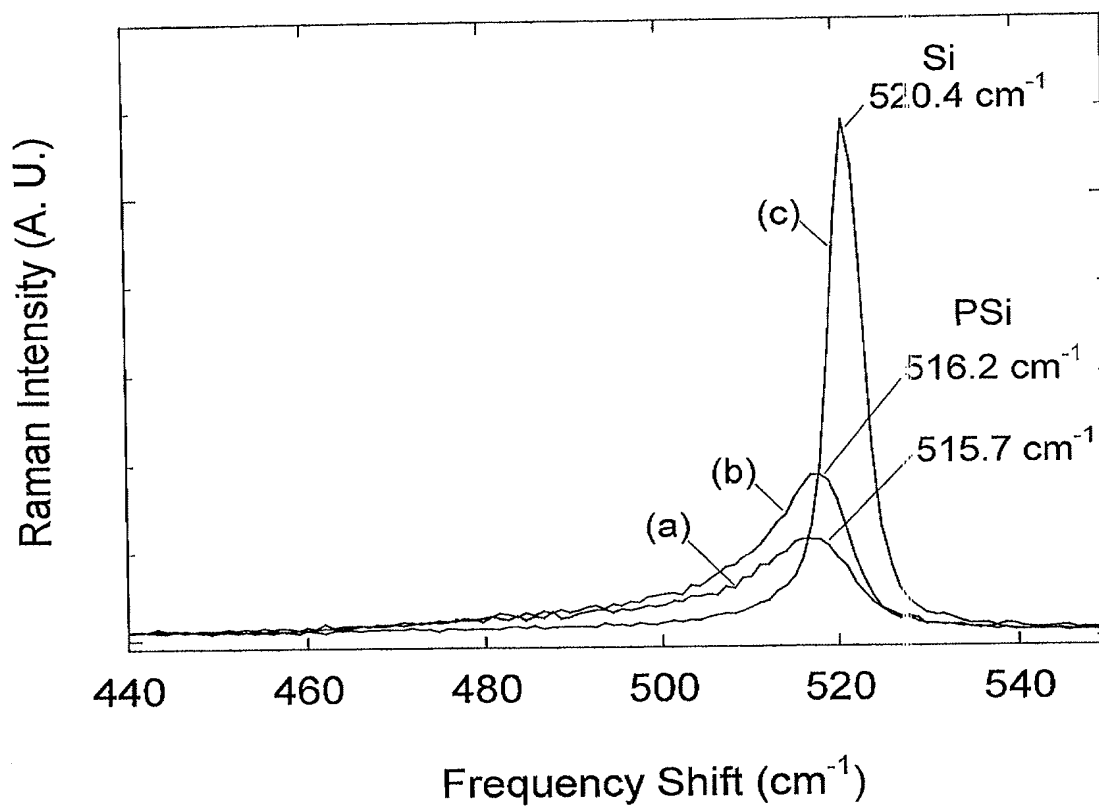


Figure 6

EXHIBIT 2

Pickled Luminescent Porous Silicon

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Ideal passivation of H-terminated light-emitting porous silicon (PSi) by the formation of covalently-bonded organic monolayers has been achieved by the thermally-induced reaction of freshly prepared PSi surfaces with alkenes and aldehydes. Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and X-ray photoelectron spectroscopy (XPS) results are consistent with the formation of oxide free organic monolayers attached covalently to the surface. Auger profiles performed on these modified PSi samples show a constant atomic concentration of carbon (and oxygen in the case of the aldehyde modified surfaces) from the top to the bottom of the pores indicating homogeneous incorporation of organic molecules on the internal surface of the PSi. The functionalized surfaces exhibit the same intensity and peak energy of the photoluminescence (PL) peak compared to the initially observed PL of the as-anodized PSi. These organic derivatized surfaces have an unprecedented ability to stabilize PSi photoluminescence. The surfaces are very resistant against oxidation even when steam treated at 70°C for several weeks, a treatment that completely destroyed hydrogen-terminated PSi. Ageing in ambient air for several months has no effect on the PL. This "pickling" process is thus highly effective in retaining the desired properties of hydrogen-terminated light-emitting PSi such as wavelength tuneable PL and high quantum efficiency, and, significantly, lends itself to further chemical modification for integration into chemical or biochemical sensors.

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Porous silicon (PSi), which has generated world-wide interest because of its tuneable electro and photoluminescent properties, is a material that was discovered about 40 years ago, during electropolishing studies of silicon in HF solutions (1). It was originally investigated for applications in semiconductor-on-insulator technologies (2). The more recent discovery of the visible photoluminescence (PL) of PSi under UV excitation, at room temperature (3), has led to considerable interest in the possibility of applications in silicon-based optoelectronics, which have been severely constrained by the weak infrared luminescence of indirect band-gap bulk silicon (4). Other significant applications based on electrical and/or optical measurements for sensing chemical (5) and biochemical (6) species have been demonstrated using PSi.

Porous silicon is composed of nano to micro-size structures with a high surface area that can be prepared from n- or p-doped silicon by chemical or electrochemical etching in HF-based solutions. The pore size and porosity can vary over a wide range depending on the electrochemical parameters (composition of the etching solution and current density), the doping level and type and the surface orientation of the silicon wafer (7). Different forms of PSi with tuneable and efficient room-temperature light emission have been prepared (8, 9). However, the origin of the PL is a subject of controversy and numerous models have been proposed in an attempt to explain this phenomenon (2). The as-prepared PSi surfaces are terminated with a covalently-bonded monolayer of hydrogen (10). Even though the hydrogen termination offers good electronic passivation of the surface (11), this monolayer does not fully protect the PL against the quenching effect of surface adsorbates and suffers from its long term instability (12); it degrades slowly upon exposure to ambient air. In fact, the silicon-hydrogen bond reacts slowly with oxygen or moisture, a process which may be accelerated under illumination, to form a sub-monolayer of oxide (13). This transformation results in the degradation of the electronic quality and the photoluminescence properties of the PSi (loss of PL or a colour change in the visible range). Air-oxidized PSi exhibits a stable red PL under UV excitation, independently of the original colour, as a result of the structural changes in the porous layer. In fact, the blue PL observed in oxide free PSi of high porosity is very sensitive to air and its spectrum shifts from the blue to red upon exposure to air for only few seconds (8). In order to prevent this evolution and to control the stability of the original PL, proper chemical and electronic termination of the surface, limiting the presence of midgap states which act as nonradiative recombination centers,

is necessary. Many attempts have been made in the past to stabilize the hydrogen-terminated surface and to reach a high efficiency of the PL. Methods based on thermal nitridation (14), halogenation (15) and metal incorporation into the pores (16) have been tested. Oxidation of the hydrogen-terminated surface was proposed as a very good alternative to stabilize the surface and preserve the PL. However, the luminescence properties are extremely sensitive to the experimental conditions which must be very carefully controlled. Thermal oxidation of PSi is one of the most common techniques for the preparation of a stable photoluminescent material, but the resulting red PL is due to oxygen related defects and is essentially non-tuneable (17). In addition, a blue emission is observed after storage in ambient air of the thermally oxidized PSi (18). This blue PL is assigned to organic contamination (hydrocarbon) and could be removed by high-temperature annealing (19). A nondegrading PL from PSi containing Si-Fe bonds was recently produced by a hydrothermal method using hydrofluoric acid and ferric nitrate aqueous solution (20), but iron is a "poison" to silicon microelectronics.

Another alternative for surface passivation is growth of organic monolayers by replacing the hydrogen atoms on the surface with organic molecules. Several methods for the formation of organic monolayers covalently-bonded to both flat and porous silicon surfaces have been reported (21). Recently, we have shown that organic-modified silicon surfaces of single crystal Si(111) through silicon-carbon (Si-C) (22) and silicon-oxygen (Si-O-C) (23) bonds are remarkably stable in different organic and aqueous solutions.

Our strategy is based on the chemical modification of the PSi surfaces by formation of stable covalently-bonded Si-C and Si-O-C. We have explored the hydrosilylation reaction of the silicon hydride-terminated surfaces with unsaturated reagents such as alkenes and aldehydes. Because of the known stability of the Si-C and Si-O-C bonds in molecular organosilicon chemistry, organic monolayers formed through these bonds are expected to be more robust and the resulting organic monolayers should be more resistant to ageing and thus prevent the PL degradation upon long storage in ambient air or even in harsh environments.

Direct reaction of freshly prepared PSi surfaces with 1-decene and alkyl aldehydes (octyl and decyl aldehydes) takes place at an elevated temperature (24) to give organic derivatized surfaces containing Si-C and Si-O-C bonds respectively (25). The reaction pathway of these transformations is shown in Figure 1.

Figure 2a displays a diffuse reflectance infrared Fourier-transform spectrum (DRIFTS) for the freshly prepared PSi substrate. The spectrum exhibits absorptions for Si-H_x stretches around 2117 cm⁻¹ and a Si-O-Si (due to interstitial oxygen in the silicon lattice) stretch at 1031 cm⁻¹, and deformation peaks associated with Si-H_x at 918, 665 and 630 cm⁻¹. After reaction of the PSi with 1-decene for 16 hours at 115^oC, the DRIFT spectrum (Figure 2b) reveals the presence of additional peaks at 2857-2960 cm⁻¹ due to the C-H stretching modes of the alkyl chain and δ(C-H) methylene and methyl bending modes at 1470 and 1367 cm⁻¹. There is no apparent increase of the peak at 1031 cm⁻¹ indicating that the reaction takes place without any oxidation of the surface, as reported by Houlton et al. (24). A similar infrared spectrum was obtained when the as-anodized PSi samples were allowed to react with octyl and decyl aldehyde at 85^oC for 16 hours, with an additional peak centered at 1069 cm⁻¹ that is consistent with the formation of Si-O-C bonds (Figure 2c).

Figure 2d indicates that most of the hydrogen on the PSi surface has reacted with the C=O double bonds (a similar result is obtained from the reaction of the alkene). This result is corroborated by the negative bands for the Si-H_x stretch modes around 2117 cm⁻¹ and the Si-H₂ scissors mode at 915 cm⁻¹. This observation implies a hydrosilylation reaction that consumes Si-H bonds (preferentially SiH₂ and SiH₃) rather than cleaving Si-Si bonds as reported for the thermal reaction of alcohols (26), Grignard (27) and alkyl lithium (28) reagents with PSi. The DRIFT spectrum indicates the presence of unreacted Si-H bonds remaining on the surface after the thermal modification, which is a consequence of the steric hindrance introduced by the organic molecules on the surface and the fact that the diameter of the alkyl chain is greater than the Si-Si spacing. Prolongation of the reaction times does not increase the coverage.

X-ray photoelectron spectroscopy (XPS) analysis of the modified surfaces showed a significant increase in the carbon and oxygen (for aldehyde functionalized surfaces) signals compared to the freshly prepared surfaces. The XPS spectrum of the modified substrate with 1-decene contains peaks due to silicon Si_{2p} (99 eV) and C_{1s} (285 eV). PSi samples derivatized with decanal exhibit the same peaks due to Si_{2p} and C_{1s}. These spectra are characterized by additional small C_{1s} and Si_{2p} peaks chemically shifted to higher binding energies, as expected for the respective carbon-oxygen (C-O) and silicon-oxygen (Si-O-C) linkages. No silicon oxide peak, which would appear near 103 eV, was apparent. Thus these surface transformations occur without any conventional oxidation of the silicon surface.

Auger profiles recorded on the modified samples show a constant atomic concentration of carbon without oxygen (below the detectable limit) from the top to the bottom of the pores for the surface reacted with 1-decene. The amount of Si detected was consistent with a 70% porosity. Similarly, a constant atomic concentration of both carbon and oxygen was observed in the aldehyde modified surfaces. This result argues for the uniform chemical attachment of organic molecules throughout the internal surfaces of the PSi.

The Raman spectrum (29) of a freshly prepared PSi sample consists of a weak band at 520 cm^{-1} due to the crystalline silicon substrate and a broad band centered at 510 cm^{-1} due to the distribution of silicon crystallites of nanometer size that comprise the PSi layer. As the same PSi Raman peak was observed after functionalization of the surface, the integrity and size of the pores remain unchanged after such treatments. Thus the thermal addition of alkenes and aldehydes to PSi does not induce any chemical etching, a consequence of Si-Si bond cleavage.

When exposed to various treatments, these surfaces are found to be very robust and showed an excellent stability in different aqueous and organic solutions at room temperature and in boiling solvents (boiling chloroform, 1.2 N aqueous HCl at 70°C). The chemical stability is not affected even in harsh environments such as aqueous HF solutions at room temperature. These observations suggest very efficient chemical passivation of the internal surface. The hydrophobic character of the alkyl chains tends to exclude polar molecules such as water.

Typical PL spectra of the modified surfaces (30) are shown in Figure 3A. The functionalized samples exhibit an orange-red photoluminescence comparable to the freshly prepared sample and characteristic of 70% porosity (2). No apparent peak shift was observed after modification. The intensity is not greatly affected by the organic monolayer. Samples modified with octanal showed only a very slight decrease of the intensity when compared to the samples derivatized with a C_{10} alkene or aldehyde. Ageing in ambient air has no effect on the PL spectrum even after 2 months. Aggressive steam treatment (31) for three days led to a very slight change in the PL intensity consistent with the effective chemical passivation of these surfaces (see above). Amazingly, six weeks ageing in steam resulted in only a small increase in the PL intensity and had no effect on the emission maximum. The modified samples exhibited an increase in the PL intensity of about three times when compared to the original PL measured just after chemical modification (Figure 3B). On the other hand, the PL of the as-anodized sample red shifted and the intensity was increased by a factor of 50, after the same steam treatment

(Figure 3C). Maruyama et al. (32) reported a similar ageing effect on the PL intensity of as-anodized PSi in ambient air and assigned this change to a gradual oxidation of the PSi skeleton. Our results point to unprecedented high stability of the alkene and aldehyde passivated surfaces.

To understand the ageing effect on the PL intensity of the modified samples and the hydrogen-terminated PSi, Raman and DRIFT spectroscopy have been used as tools to monitor the intrinsic properties of the porous layer. For the functionalized surfaces, PSi and SiH_x Raman peaks (Fig. 3) remain unchanged, having the same features seen in the initially modified surfaces (before ageing). The appearance of a Si-O-Si stretch in the DRIFT spectrum and of a new peak at 103 eV in XPS suggest that the increase in PL intensity is due to the formation of a very small amount of silicon oxide during the ageing process (without any apparent loss in the organic layer). Similar spectroscopic results were reported by Chazalviel et al. for the electrochemically methylated (33) and methoxylated (34) PSi surfaces. However, in this case there was a slight blue shift in the PL spectrum and the PL was lost after ageing the methoxylated surface in air for several days. More recently, Buriak et al. (35) have studied the ageing effect on the PL fatigue of PSi surfaces modified with 1-dodecene (prepared by a hydrosilylation reaction catalyzed by EtAlCl_2), soaked in HF/EtOH (30 min at room temperature) and boiled in aerated KOH/EtOH solutions (pH = 10, 2 hours). They found that the PL of samples treated both ways decay faster than a freshly prepared H-terminated PSi sample.

In contrast to the organic derivatized surfaces, the DRIFTS and Raman spectrum of the hydrogen-terminated surface reveal a drastic change in the integrity of the pores after ageing. Only the Raman peak centered at 520 cm^{-1} due to the signal from the underlying bulk silicon was observed. Both the broad feature centered at 510 cm^{-1} due to the porous layer and the SiH_x peak were absent. The SiH_x stretch present in the H-terminated surface centered at 2117 cm^{-1} in DRIFTS shifted to 2249 cm^{-1} (characteristic of $\text{O}_3\text{Si-H}$) and was accompanied by the appearance of an intense band at 1114 cm^{-1} (corresponding to the Si-O-Si stretch). The high intensity of the Si-O-Si peak and the loss of the Raman peaks is attributed to the transformation of the PSi layer into a transparent oxide layer, which explains the bright PL.

In conclusion, we have demonstrated that this pickling of PSi surfaces by the bonding of organic monolayers provides ideal chemical and electronic passivation leading to unprecedented long term stabilization of the room temperature PL. The method is easy to carry out and highly effective for the passivation of hydrogen-terminated PSi surfaces. The presence of oxygen in the

derivatized samples with aldehydes does not introduce any shift in the PL nor introduce the defect states evident in oxidized PSi.

Advantages of this approach arise from its application for the stabilization of the PL resulting from PSi of any porosity. Because it is a nondestructive method (i.e. it does not etch the internal surface), the structural integrity of the PSi layer is retained allowing the possibility that it can be used for the preparation of efficient, tuneable, and stable light-emitting devices. In a broader sense, the ability to design and control the interface between inorganic and organic materials will open the door to new devices and applications. For example, organic monolayers formed from saturated aliphatic chains can serve, in principle, as low dielectric materials. The ability to control the thickness of these films, simply by choosing the appropriate alkyl chain length, may allow these materials to serve as useful replacements for traditional gate oxides in hybrid semiconductor/organic devices. The introduction of conjugated molecules into the monolayers would allow the conductivity across the film to be modulated. Thus, it is conceivable that one could drive a reasonable current across these organic passivated surfaces. Finally, the large variety of compatible organic functionalities offer enormous potential for wide-ranging applications in chemical and biochemical sensing. The challenge is to devise simple design principles for the integration of molecular recognition sites which can modify the electronic and/or optical properties of inorganic materials. Some of the advances reported here are key to that success.

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25. Porous silicon samples were prepared by electrochemical etch of single side polished (100) oriented p-type silicon wafers (B-doped, 1-1.05 ohm-cm resistivity) in a 1:1 (v) pure ethanol and 48% aqueous HF for 8min at a current density of 5mA/cm². Atomic force microscopy in contact mode showed that PSi films prepared in this way are 2.5 to 3 μ m thick with a pore diameter around 5 nm. The porosity was evaluated using the X-ray reflection technique and found to be 70%. The modification of the PSi surfaces was achieved by immersing the freshly prepared samples in a deoxygenated solution of neat alkene or aldehyde at 85°C for 16 hours. The excess of unreacted and physisorbed reagent was removed by rinsing, at room temperature, with tetrahydrofuran and 1,1,1-trichloroethane and then dried under a stream of nitrogen prior to PL measurements.
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30. Raman and PL measurements were performed at room temperature using 30 mW of Ar⁺ laser excitation at 457.9 nm. Special care was taken to avoid laser heating of the sample, which was immersed in helium gas.
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36. We thank G. I. Sproule and J.-M. Baribeau for the Auger and X-ray measurements, respectively.

Figures caption :

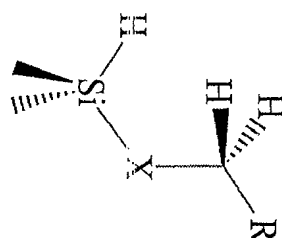
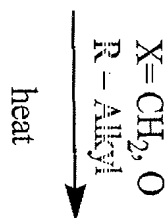
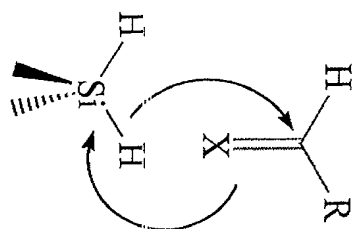
Figure 1: (a) The thermal reaction of an alkene ($X=CH_2$) and an aldehyde ($X=O$) with PSi leading to the formation of Si-C and Si-O-C bonds respectively and migration of the hydrogen (Si-H) from the PSi surface to the unsaturated carbon. The hydrosilylation reaction takes place at $115^{\circ}C$ with 1-decene and at $85^{\circ}C$ for octyl and decyl aldehydes. (b) Schematic representation of the thermal addition of 1-decene to PSi surfaces. The yellow atoms are silicon, the dark blue are hydrogen and the light blue are carbon. Organic molecules readily migrate into the pores and react with the internal silicon hydrides ($Si-H_x$). The only limiting factor in fully substituting the hydrogens by organic molecules is the steric hindrance.

Figure 2: Diffuse reflectance infrared Fourier-transform spectra for (a) freshly prepared PSi before functionalization and PSi derivatized with (b) 1-decene, (c) decylaldehyde and (d) a difference DRIFT spectrum of the functionalized PSi with decylaldehyde. No features were observed at higher wavenumbers ($3200-4000\text{ cm}^{-1}$) in any samples.

Figure 3: Steady-state room temperature PL spectra of **A:** (a) as-anodized PSi before functionalization, (b) derivatized PSi with octaldehyde, (c) decylaldehyde, and (d) 1-decene, **B:** (a) freshly prepared 1-decene modified PSi surface and (b) after steam treatment for six weeks, and, **C:** (a) as-anodized porous silicon, (b) after steam treatment for six weeks, and (c) Figure 3(a) scaled up by 50. The sharp lines at high energy are Raman peaks of PSi and of SiH_x (at 2100 cm^{-1}).

Canada

(a)



(b)

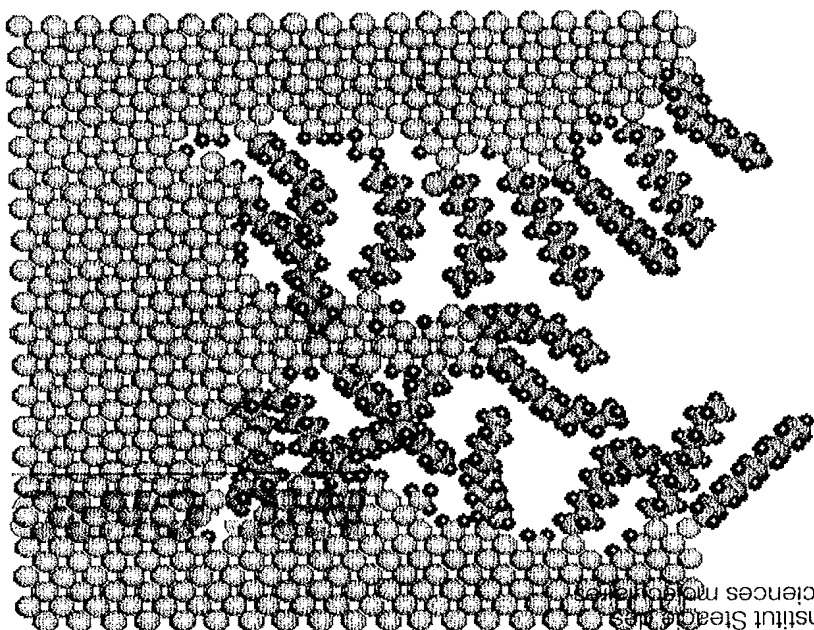
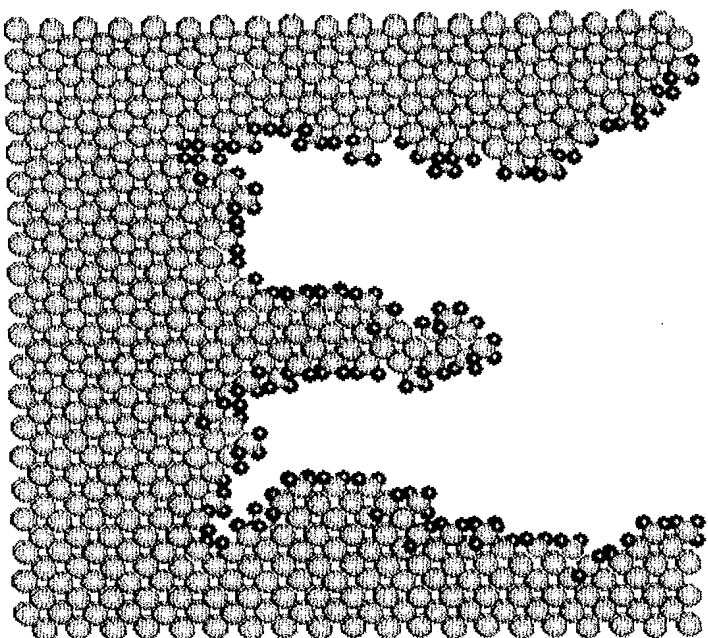


Figure 1

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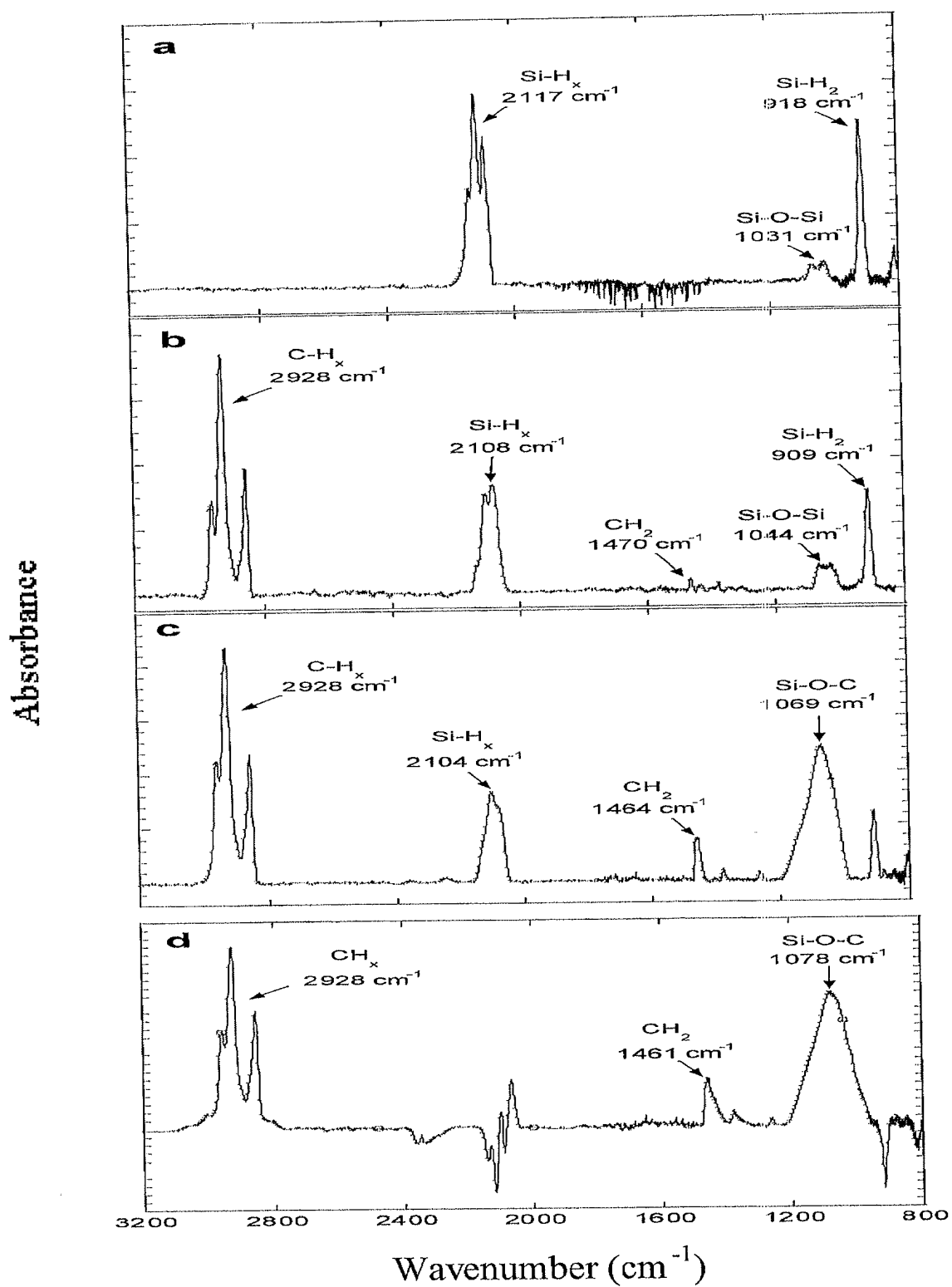


Figure 2

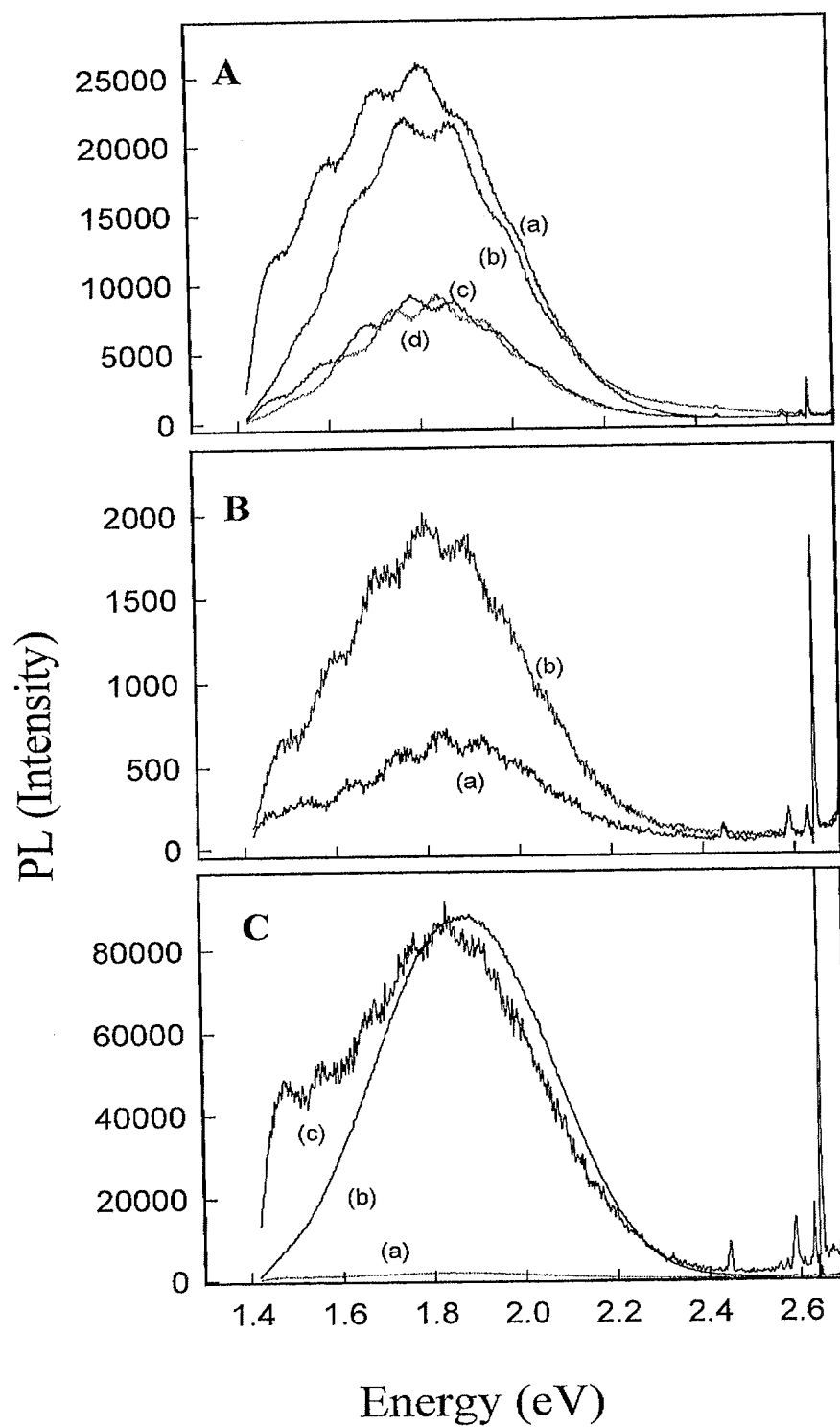


Figure 3